OPTICAL AND MECHANICAL PROPERTIES OF TAPIOCA STARCH /WATER / TRITON X-100/ AEROSIL®200 LYOTROPIC LIQUID CRYSTAL

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ABSTRACT

This work focus on the study of the optical and mechanical properties of Tapioca Starch/ H_2O/ Triton X-100/ Aerosil®200 lyotropic liquid crystal(LLC). Polarize Optical Microscopy, Rheology and Small-and-Wide Angle X-ray Scattering method was used to determined the properties of the LLC. Fifty three samples with different composition ratio were prepared and characterized. The viscosities of the samples were studies at different temperature of 15, 25 and 45˚C in order to study the effect of temperature on the samples. Ternary diagram obtain from this work show that four phases occur in the composites or samples, namely Lamellar, Hexagonal, Micellar and Discotic. The spacing lattice (d), of the composites was in the range of 76.72Å to 122.26Å. The study shows that at low temperature, the liquid acts as a lubricant and the lyotropic flows easily while at higher temperature, the liquid is unable to fill the gaps created between particles, and friction greatly increases, causing an increase in viscosity. The Tapioca Starch/ Triton X-100/ water/ Aerosil®200 LLC prepared in this work produce similar properties of shear thickening fluid.

PENCIRIAN SIFAT-SIFAT OPTIKAL DAN MEKANIKAL BAGI KANJI UBI KAYU/ TRITON X-100/ AIR/ AEROSIL® 200 CECAIR KRISTAL LIOTROPIK

ABSTRAK

Kajian ini difokuskan pada pencirian sifat-sifat optical dan mekanikal kombinasi kanji Ubi Kayu/Triton X-100/ air dan Aerosil®200 sebagai cecair kristal lyotropic dengan mengunakan Mikroskop Optik Polarisi, keadah Pengaliran dan keadah Small-dan-Wide Angle Hamburan sinar-X untuk menentukan pencirian sifat-sifat cecair kristal liotropik. cecair kristal liotropik dihasilkan dengan mencampur kombinasi kanji ubi kayu/Triton X-100/ air dan Aerosil®200 dari sukatan yang berbeza setiap satu bahan dan dengan menggunakan pengacau magnetik bagi menyebatikan larutan. Lima puluh tiga sampel dengan komposisi yang berbeza telah dianalysis. Kajian pada kelikatan sampel dijalankan pada suhu yang berbeza 15, 25 dan 45 ˚ C untuk mempelajari pengaruh suhu terhadap sampel. Data yang diperolehi dari Ternary diagram menunjukkan terdapat empat fasa di dalam komposit atau sampel, iaitu fasa lamellar, fasa hexagonal, fasa micellar dan fasa diskotik. Ruang kisi(d), dari komposit sample yang diperolehi adalah 76.72Å hingga 122.26Å. Keputusan kajian menunjukkan bahawa pada suhu rendah, liotopik cair seperti pelincir dan pengaliran liotropik cair sedangkan pada suhu yang tinggi, cecair tidak dapat mengisi jurang yang diciptakan antara zarah, dan gesekan semakin meningkat, menyebabkan peningkatan kelikatan. Pencirian sifat-sifat kombinasi Kanji Ubi Kentang/ Triton X-100 / air / Aerosil®200 LLC yang dijalankan dalam kajian ini menunjukkan terdapat ciri-ciri yang sama dengan luncurkan penebalan cecair.

CONTENTS

LIST OF TABLE

LIST OF FIGURE

LIST OF ABBREVIATIONS

Abbreviations

POM	Polarization Optical Microscope
SWAXS	Small and Wide Angle X-ray Scattering
LLC	Lyotropic Liquid Cystal
d	Spacing Lattice

LIST OF APPENDIX

CHAPTER 1

INTRODUCTION

This chapter explains on the overall and research objectives of the study. This chapter is divided by five parts which are part 1.1 is about the background of the study, 1.2 problem statements, 1.3 shear thickening fluid, 1.4 ternary diagram, 1.5 objectives of the research and 1.6 scope of research, 1.7 Limitations of the Research, and 1.8 Organizational Outline.

1.1 Background of the study

What is liquid crystal? There are three common states of matter that most people know about: solid, liquid, and gas. Liquid crystal is a state that the molecules in solid exhibit both positional and orientation order, in other words; the molecules are constrained to point only certain directions and to be only in certain positions with respect to each other. In liquids, the molecules do not have any positional or orientation order, the direction of the molecules point and their positions are random.

The liquid crystal phase exists between the solid and the liquid phase the molecules in liquid crystal do not exhibit any positional order, but they do possess a certain degree of orientation order. The molecules do not all point the same direction all the time. They merely tend to point more in one direction over time than other directions (Farn, 2006).

Liquid crystals come in three basic classifications: thermotropic, metallotropic and lyotropic. The phase transitions of thermotropic liquid crystals depend on temperature, a mesophase formed by dissolving an amphiphilic mesogen in a suitable solvent, under appropriate conditions of concentration, temperature, and pressure. The essential feature of a lyotropic liquid crystal (LLC) is the formation of molecular aggregates or micelles as a result of specific interactions involving the molecules of the amphiphilic mesogen and those of the solvent while those of LLC depend on both temperature and concentration. This research will focus on LLC. LLC were actually discovered long before their thermotropic counterparts were known. In 1850, their texture was noticed in a mixture of myelin and water. Figure 1.1 depict a myelin is a fatty material, composed chiefly of lipids and lipoproteins that enclose certain axons and nerve fibers. However at the time of discovery, the significance of liquid crystals was not understood, so most research has been done only to the thermotropics. Just fairly recently studies on LLC have begun to catch up (Farn, 2006).

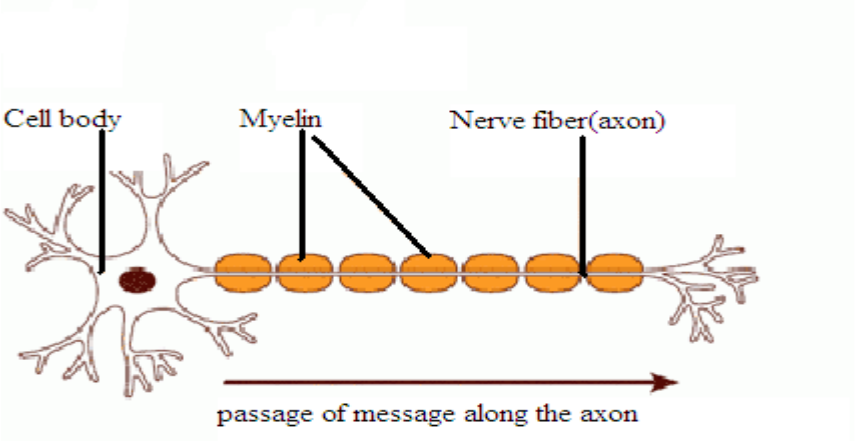

Figure 1.1: Structure of Myelin (Lorenzos.,2001)

LLC are found in countless everyday situations. Soaps and detergents form LLC when they combine with water. In the kitchen, cake batters may harbor the liquid crystals as well. Most importantly, biological membranes display LLC behavior. This research explored the potential use of surfactant-containing systems, detailed rheological and characterization that had become increasingly important, for example in the design of pumping, agitation and mixing operational units. Moreover, it also helps one to establish theoretical understanding of the relationships between viscosity properties and the microstructures (Farn, 2006).

At low concentrations, the solution looks like any other particles of solute distributed randomly throughout the water. However when the concentration of solution get high enough, the molecules begins to arrange themselves in hollow spheres, rods, and disks called micelles. In some reactions, the type of micelle affects the reaction rate, most likely because the parts of the molecule involved in the reaction are more likely to be exposed in some formations than in others. The surface of a micelle is a layer of polar heads dissolved in the water, while the inner portion consists of hydrophobic tails screened from the water by the hydrophilic heads. Micelles come in varied sizes, but the smallest ones have a diameter about twice as long as the length of a hydrocarbon chain with all trans-bonds. As the weight concentration of amphiphile increases, the micelles become increasingly able to dissolve no-polar substances. When this occurs, the micelles become large and swollen. If they reach a large enough size, the solution becomes cloudy and is called an emulsion. At lower concentrations, the swollen micelles are not large enough to interfere with light, but they are still extremely stable and exist in equilibrium. This phase is referred to as a microemulsion (Farn, 2006).

Figure 1.2 depicts the arrangement and structure of micellar while Figure 1.3 depicts the arrangement of polar heads and hydrophobic tails in micellar.

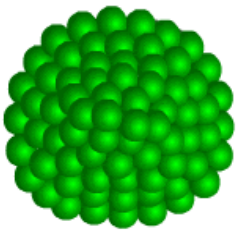

Figure 1.2: Spherical micelle
(Lorenzos.,2001)

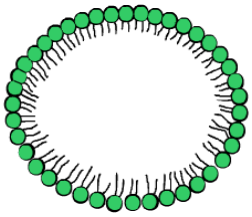

Figure 1.3: Crossection
(Lorenzos.,2001)

A liquid crystalline material is called lyotropic if phases having long-ranged orientation order are induced by the addition of a solvent. Historically the term was used to describe materials composed of amphiphilic molecules. Such molecules comprise a water-loving (hydrophilic) head-group (which may be ionic or non-ionic) attached to a water-hating (hydrophobic) group. Typical hydrophobic groups are saturated or unsaturated hydrocarbon chains (Shao et al, 1998). Elisabeth Andreoli de Oliveira (1998), state that Lyotropic systems are obtained by the dispersion of amphiphilic molecules in water, that assembly in anisotropic aggregates called micelles. The micelles can be seen as biaxial objects, with typical dimensions of (100 x 70 x 30) Å. The phase transitions in lyotropics occur by temperature or concentration variations.

According to Yuan Ming Huang and Wei-Wei Liu (2010), a LLC consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In the lyotropic phase, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic liquid crystals, these lyotropic have another degree of freedom of concentration that enables them to induce a different of variety phase.

The content of water or other solvent molecule changes the self-assembled structure. At low amphiphile concentration, the molecules will be dispersed random without any ordering. At slightly higher concentration, the molecule will spontaneously assemble into micelles or vesicles. These spherical objects do not order themselves in solution, however at higher concentration, the assemblies will become ordered. A typical phase is a

hexagonal columnar phase, where the amphiphiles from long cylinder that arrange themselves into roughly hexagonal lattice. This is called the middle soap phase. At still higher concentration, a lamellar phase may form where in extended sheets of amphliles are separated by thin layer of water (Huang and Liu, 2010).

In this research focus on investigate the mechanical properties and the characterization of LLC formed from different concentration of Tapioca starch/ H_2O/ Triton x-100($C_{14}H_{22}O(C_2H_4O)_n$)/ Aerosil®200 (hydrophilic fumed silica) by using Polarizing Optical Microscope(POM) to determined the presence of liquid crystal phases namely as lamellar, cubic and hexagonal phase. Non liquid crystalline phases also expected such as nanoemulsion and micellar solution.

Small and Wide Angle X-ray Scattering (SWAXS) will be used for further characterization of the phases.

1.2 Problem statement

A dilatants (also termed shear thickening) material is one in which viscosity increases with the rate of shear. Such a shear thickening fluid, also known by the acronym STF, is an example of a non-Newtonian fluid (Cheremisihoff and Nicholas P. 1988).

The dilatants effect occurs when closely packed particles are combined with enough liquid to fill the gaps between them. At low velocities, the liquid acts as a lubricant, and the dilatants flows easily. At higher velocities, the liquid is unable to fill the gaps created between particles, and friction greatly increases, causing an increase in viscosity. (Cheremisihoff and Nicholas 1988). This can readily be seen with a mixture of cornstarch and water, which acts in counterintuitive ways when struck or thrown against a surface. Dilatants materials have certain industrial uses due to their shear thickening behavior. For example:

1.2.1 Traction control

Some all wheel drive systems use a viscous coupling unit full of dilatants fluid to provide power transfer between front and rear wheels. On high traction road surfacing, the relative motion between primary and secondary drive wheels is the same, so the shear is low and little power is transferred. When the primary drive wheels start to slip, the shear is increasing, causing the fluid to thicken. As the fluid thickens, the torque transferred to the secondary drive wheels increases proportionally, until the maximum amount of power possible in the fully thickened state is transferred (Andrew Trevitt, 2009).

1.2.2 Body armor

Various corporate and government entities are researching the application of shear thickening fluids for use as body armor. Such a system could allow the wearer flexibility for a normal range of movement, yet provide rigidity to resist piercing by bullets, stabbing knife blows, and similar attacks. The principle is similar to that of mail armor, though body armor using dilatants would be much lighter. The dilatants fluid would disperse the force of a sudden blow over a wider area of the user's body, reducing the blunt force trauma. However, against slow attacks which would allow flow to occur, such as a slow but forceful stab, the dilatants would not provide any additional protection. (Victoria Gill, 2010).

Shear thickening fluid already been study by many scientists because of their properties and application in many industries. In addition, according to Barnes, (1989), shear-thickening has been considered a problem in many industrial applications including the mixing, coating, milling, or spraying of these fluids. However, it is intended, in this research, to use the results found to control shear thickening in a manner that would be beneficial to our energy shunting system. This research is to investigate the properties of tapioca starch based shear thickening fluid in term of shear (in a certain selected region) Triton X-100, Water and Aerosil®200 phases (liquid crystals, micellar and nanoemulsions).

1.3 Significant of the research

A shear-thickening fluid (STF)**,** behaves like a solid when it encounters mechanical stress or shear**.** In other words, it moves like a liquid until an object strikes or agitates it forcefully. Then, it hardens in a few milliseconds. This is the opposite of a shear-thinning fluid**,** like paint, which becomes thinner when it is agitated or shaken.

By examined a solution nearly equal parts of starch and water, we can see shear-thickening fluid looks like. Shear-thickening fluids are concentrated colloidal suspensions composed of non-aggregating solid particles suspended in fluids. These suspensions have the property of increasing the fluid viscosity with increasing shear rate. In addition, this increased viscosity is seen as being both fields activated, due to the dependency on shearing rate, as well as reversible **(**Jose G. Ramirez, 2004). Colloid made of tiny particles suspended in a liquid. The particles repel each other slightly, so they float easily throughout the liquid without clumping together or settling to the bottom. But the energy of a sudden impact overwhelms the repulsive forces between the particles; they stick together, forming masses called hydroclusters. When the energy from the impact dissipates, the particles begin to repel one another again. The hydroclusters fall apart, and the apparently solid substance reverts to a liquid.

1.4 Ternary phase diagram

In studying the characterization and rheological of lyotropic liquid crystal, the ternary phase diagram is used to plot liquid crystal phase in three different temperature in order to understand the system of liquid crystal during the research. A basic study not only can give a better view at which concentration of liquid crystal phase and emulsifiers to formulate gels, liquid crystalline products, micellar solution, it also provide information like at which area where the separation will occur.

1.5 Objective

1. To investigate the rheological properties of tapioca starch based shear thickening fluid in term of shear (in a certain selected region) Tapioca Starch/ H_2O/ Triton X-100/ Aerosil®200 phase (liquid crystals, micellar and nanoemulsions).

2. To investigate the structural properties of selected composition of Tapioca starch/ H_2O/ Triton X-100/ Aerosil®200 using POM and SWAXS.

3. To construct the Ternary Phase Diagram of Tapioca starch/ H_2O/ Triton X-100/ Aerosil®200.

1.6 Scope of research

In this project the optical and mechanical properties of Tapioca starch/ H_2O/ Triton X-100/ Aerosil®200 system was investigated. The POM had been utilized for optical properties characterization. It had been the first step to determine the phases of liquid crystals. POM utilizes polarized light to form a highly magnified image phase of LLC. POM plays an important role in crystallography. A POM differs from a conventional light microscope in a number of ways. A POM has a pair of polar (polarizing devices) in the optical train. The first polar (polarizer) defines the initial plane of polarization for light entering the microscope and is located between the illuminator and the condenser. The other polar (analyzer) is usually placed between the objective and the ocular tube and defines the plane of polarization of the light reaching the ocular. One or both must be accurately rotatable about the optical axis of the instrument. Usually the analyzer is also removable from the optical path.

SWAXS had been used to confirm the phases and also to determine the spacing (d) of each sample. By used SWAXS probes structure in the nanometer to micrometer range by measuring scattering intensity at scattering angles 2θ close to 0°or large than 5˚. X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials (Guodong Zhang et al., 2007).

Rheometer used to study the mechanical behavior of each sample from the system. The liquid is placed within the annulus of one cylinder inside another. One of the cylinders is rotated at a set speed. This determines the shear rate inside the annulus. The liquid tends to drag the other cylinder round, and the force it exerts on that cylinder (torque) is measured, which can be converted to a shear stress. By the knowledge's and results that we will get at the end of this project, a variety of applications that we can do based on the LLC such as nanoparticles synthesis, cosmetics, food and beverages, pharmaceuticals and shear thickening fluid (STF) (Erica E et al., 2009).

In this research the Ternary Phase Diagram is to determine the phase of LLC using different concentration of Tapioca Starch/ H_2O/ Triton X-100/ constant concentration of Aerosil®200. All three materials that used in this project has been measured their concentration and weight before applied to the Ternary Phase Diagram. Aerosil®200 and Triton X-100 had added into the Tapioca Starch as other varies factors which are studied in rheology. The flow of tapioca starch can not be characterized by a single value of viscosity (at a fixed temperature), thus there will be several sample has been prepared. Result from this result can be used to vary application in industry, such as: thickening additives**,** emulsifying additives and stabilizing additives**.**

1.7 Limitations of research

In this research, the solution Triton X-100 and Aerosil®200 are already prepared. Hence, the study of solution synthesis is not done.

1.8 Organizational outline

Chapter 1 includes the research background, problem statement, significant of the research, research objective, and scope of the research and also the limitations of the research.

Chapter 2 describe about the latest research that related to this research. In this chapter, they are focus on the shear thickening fluid, starch, surfactants, fumed silica, self assemble aggregation and LLC.

Chapter 3 describes detail about the material, instrument and research technique. It also includes sample preparation, characterizes of LLC by POM, flow and structure of LLC using Anton Paar Physica MCR 300 Rheometer and SWAXS.

Chapter 4 explains about result and discussion. Result analyzed base on ternary diagram, table, picture and graph that obtain from the experiment. Discussions are written in detail base on theory and evident from previous research.

Chapters 5 explained the overall of the research and state whether the objective of the research achieved. It also includes the recommendation for the future research.

CHAPTER 2

LITERATURE REVIEW

This chapter will explain about the studies of dye and conducting polymer layer with ITO coated glass. This chapter divided to part, 2.1 Tapioca Starch, 2.2 Aerosil®200, 2.3 Surfactants, 2.3.1 Triton X-100, 2.4 Rheology of Dilatants, 2.5 Self Assemble Aggregation and lastly 2.6 Lytropic Liquid Crystal (LLC).

2.1 Tapioca Starch

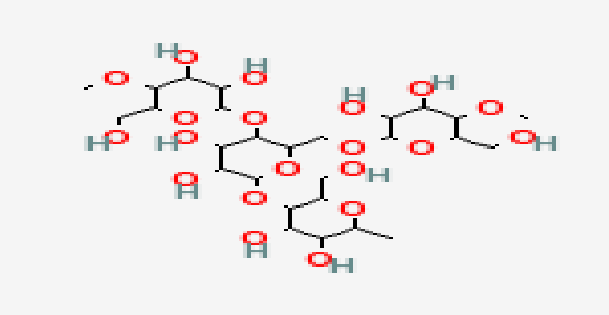

Figure 2.1: Tapioca starch structure (Self et al., 1990).

Starches are commonly added to popular foods such as soups and sauces to increase their consistency and improve mouth-feel characteristics. The thickening activity of starches results from the swelling of starch granules occurring at gelatinization temperatures (Self et al., 1990). Starch has been widely used in the food industry as an adhesive, binding, gelling and thickening agent because the pseudoplastic property of gelatinized starch at lower shear rate is important for food products by suspended starch particles and the food

does not become too viscous when mixed or poured at higher shear rates during processing (Whistler & Be Miller, 1997)

Tapioca starch obtained from cassava roots is more widely used as a thickener in the food industry compared to other starches, especially in Southeast Asia because of its high viscosity, clear appearance, and low production cost. There have been many research reports on the rheological properties of starch solutions but no published information is available on the rheological modeling of tapioca starch solutions. Depending on the range of shear rates, temperatures and concentrations, the tapioca starch suspension in water behaves as a typical dilatants system. The flow curves of the suspension at various concentrations and temperatures were obtained by using a rheometer. The flow mechanism of the suspension is explained by a structure model of starch granules in the suspension (Jeong et al., 1989).

As is well known, during storage, aggregation or recrystallization of starch biopolymers in starch granules can occur and lead to increased rigidity and syneresis affecting the texture of starch-based food products (Liu et al., 2003).

This leads to difficulty in predicting and controlling the change of physical properties of starch-based foods during the time before consumption. A well-known technique to modify viscosity/ texture or maintain desirable viscosity/ texture during storage is to blend starches with other hydrocolloids or biopolymers. When a starch/ hydrocolloid mixture is used as a texture modifier, understanding of its rheological and thermal properties is important to improve the formulation of starch-based foods (Lee et al., 2003); Yoshimura et al., 1996). Thus, many investigations on rheological and thermal properties of mixtures between starches and hydrocolloids have been performed. In general, the viscosity of a starch/hydrocolloid mixed system is much higher than that of starch or hydrocolloid alone because most biopolymers are strongly hydrophilic and compete with starch for water (Christianson et al., 1981); (Funami et al., 2005); (Shi & Be Miller, 2002).

2.2 Aerosil®200

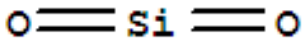

Figure 2.2: Aerosil®200 structure (Volkovinskaya et al., 2008).

Aerosil is a fumed silica product developed in 1942 by Degussa AG (currently Evonik Industries) in Germany. Aerosil is pure silicon dioxide, made from vaporized silicon tetrachloride oxidized in high-temperature flame with hydrogen and oxygen. It gives thickening effect and thixotropy by dispersing to liquid materials. Standard hydrophilic products are made of primary particles from 7 nm to 40 nm, and also these products are surface modified to hydrophobic (Volkovinskaya et al., 2008).

At this present time, Aerosil is widely uses abroad as disintegration auxiliary. Aerosil is amorphous non-porous silica with particle dimension from 4 to 40mμ. It is a very light, white powder. The surface Aerosil is hydrophilic which promotes the disintegration of the hydrophobic and improves the granulation process and the flow characteristics of the granules'. Aerosil is a good absorption medium in the tabulating of oil and moist substance and those sensitive to moisture (Volkovinskaya et al., 2008).

Fumed silica serves as a universal thickening agent, in milkshakes for example, and a anticaking agent (free-flow agent) in powders. Like silica gel, it serves as a desiccant. It is used in cosmetics for its light-diffusing properties. It is used as a light abrasive, in products like toothpaste. Other uses include filler in silicone elastomeric and viscosity adjustment in paints, coatings, printing inks, adhesives and unsaturated polyester resins. As a thickening agents substances which, when added to an aqueous mixture, increase its viscosity. They provide body and increase stability. Fumed silica materials used to thicken and stabilize liquid solutions, emulsions, and suspensions. They dissolve in the liquid phase as a colloid mixture that forms a weakly cohesive internal structure. Emulsions are part of a more general class of two-phase systems of matter called colloids.

More recently, Chellamuthu et al (2009) investigated the extensional rheology of a shear-thickening fumed silica nanoparticle suspension using a filament stretching rheometer. Below a critical extension rate, their measurements showed little strain hardening. At a critical extension rate, however, Chellamuthu et al (2009) observed a dramatic increase in the rate and extent of strain hardening of the extensional viscosity similar to the thickening transition observed in shear. Light scattering measurements showed that the extensional hardening was due to the alignment of nanoparticles and the formation of long strings of aggregates in the flow. The fumed silica particles used in their study had a fractal chain-like structure (Raghavan and Khan, 1997). One question this current study hopes to answer is whether extensional hardening can also be achieved in symmetric or nearly symmetric particles that exhibit shear thickening.

2.3 Surfactants

A surfactant molecule is formed by two parts with different affinities for the solvents. One of them has affinity for water (polar solvents) and the other for oil (non-polar solvents). A little quantity of surfactant molecules rests upon the water-air interface and decreases the water surface tension value (the force per unit area needed to make available surface). That is why the surfactant name: "surface active agent"(Farn, 2006).

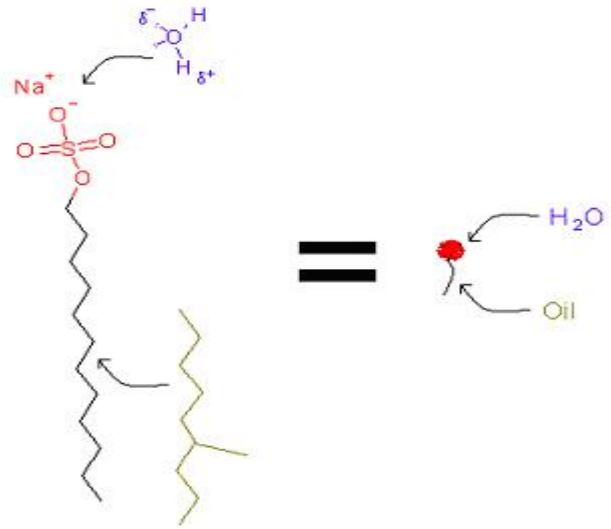

Figure 2.3: An example of surfactant molecule (SDS molecule).
The polar "head" has affinity for water and the "tail" has affinity for oil (Farn, 2006).